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A METHOD TO COMPARE THE POTENTIAL OF
A FLOWING LIQUID HYDROCARBON TO GENERATE
STATIC ELECTRICITY

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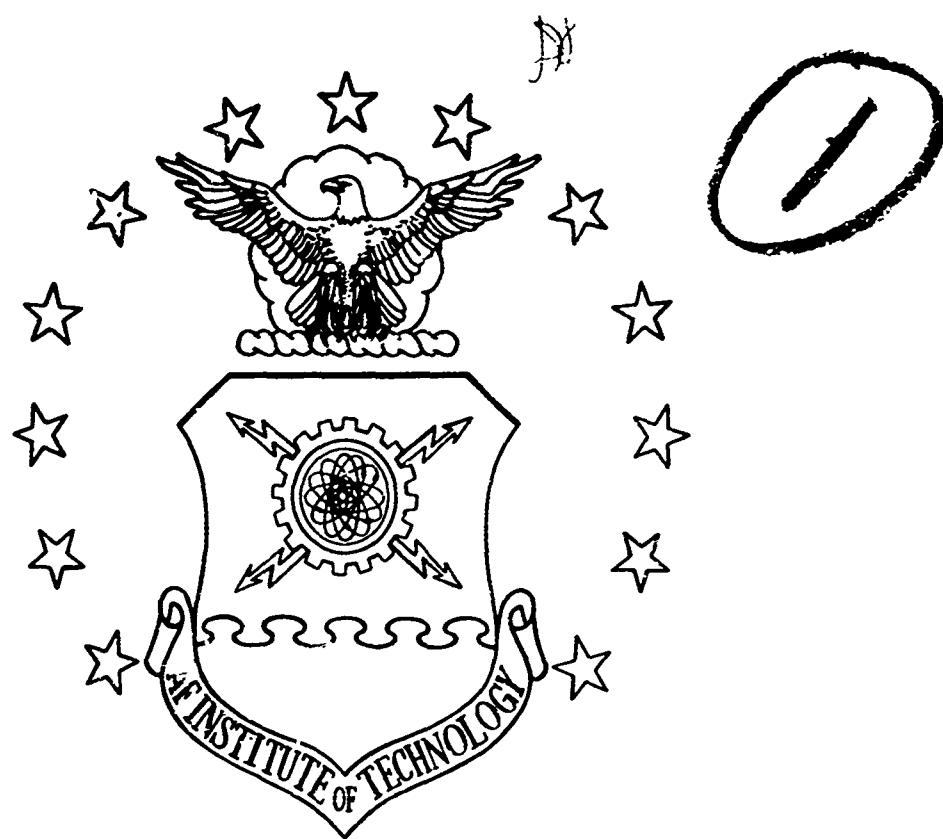
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12. ABSTRACT <p>This study examines static charge generation in hydrocarbon fuels during flow through pipes. Particular emphasis is placed on the effect of linear velocity, pipe diameter and length, and the liquid solid interface. A parameter was developed which may be of use to system designers as a basis for comparing static electric charge generating characteristics of various fuel-container material combinations. The parameter was first derived from theoretical considerations and then introduced into an equation which quantifies the charge carried by the liquid flowing in a pipeline. This equation became the basis for a model which defined the physical quantities which had to be obtained experimentally in order to evaluate the parameter.</p> <p>Laboratory scale apparatus for the measurement of conductivity and charge density in the flowing fluid was designed, constructed and instrumented. Preliminary experimental data for JP-4 fuel confirmed that this proposed apparatus and laboratory procedure could be used to evaluate the parameter and verify its validity over a wide range of velocities and pipe lengths. A by product of this work was the development of a fully guarded parallel plate conductivity cell which indicates some improvement over other designs.</p>		

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A METHOD TO COMPARE THE POTENTIAL OF
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GENERATE STATIC ELECTRICITY

THESIS

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of the Air Force Institute of Technology

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in Partial Fulfillment of the
Requirements for the Degree of

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by

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Preface

This report presents the results of an investigation of the static electricity generated by some hydrocarbons during flow through tubes of various lengths. The purpose of this research was to define a parameter and develop a method for measuring it. The parameter, which is to be used to compare the charge generating potential, is a function of the electrical and transport properties of the hydrocarbon, the pipe material and a representative dimension. Its application would provide the designer of both fixed and mobile fuel handling systems with an analytical method of establishing system criteria which reflect both safety and economy.

Throughout the course of this study, there were many people who provided help and suggestions when they were needed. My deepest appreciation is given to Dr. Harold E. Wright who not only contributed his knowledge and prior experience, but also a great enthusiasm for the project which urged me on even during periods of difficulties.

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Valcntine L. Denninger

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List of Symbols

<u>Symbol</u>	<u>Description</u>
A	Area of plates, meters ²
A_w	Wetted area of pipe, meters ²
C	Capacitance, farads
C'	Active Capacitance, farads
C_a	Capacitance of calibrated capacitor, farads
C_e	Capacitance of empty conductivity cell, farads
C_f	Capacitance of cell containing hydrocarbon standard, farads
C_R	Capacitance of receiver vessel, farads
D	Diameter of pipe, meters
e	Relative dielectric constant, dimensionless
e_H	Relative dielectric constant of hydrocarbon standard, dimensionless
e_n	Napierian logarithm base
e_0	Absolute dielectric constant of vacuum, farads/meter
f	Fanning friction factor, dimensionless
i	Current, amperes
i_s	Streaming current, amperes
I_p	Current test pipe to ground, amperes
I_R	Current receiver vessel to ground, amperes
I_s	Current source vessel to ground, amperes
j_a	Density of current issuing from wall, amperes/meter ²
j_w	Density of current from liquid to wall, amperes/meter ²
k	Conductivity, picomhos/meter

<u>Symbol</u>	<u>Description</u>
k_c	Conductivity cell constant, centimeters ⁻¹
k_e	Electrification parameter, coulomb seconds/meter ^{2.5}
χ_p	Proportionality constant to correct units
z	Length of pipe or distance between capacitor plates, meters
L	Overall pipe length, meters
n	Viscosity, kilogram/meter seconds
q	Charge in fuel at any time t, ampere seconds
q_0	Initial charge on incoming fuel, ampere seconds
Q	Total charge on capacitor, ampere seconds
Q_0	Initial charge on capacitor, ampere seconds.
r	Resistance, ohms
r'	Resistivity, ohm meter
R	Radius of pipe, meters
R_e	Reynolds number, dimensionless
s	Charging tendency, micro coulombs/meter ³
t	Time, seconds
t'	Half time value, seconds
t_1	Half time of receiver vessel, seconds
t_2	Half time of receiver vessel with capacitor shunt, seconds
T_n	Temperature subscripted to indicate location, degrees centigrade
T_{ss}	Shear stress at pipe wall, kilograms/meter second ²
V	Potential difference, volts
\bar{V}	Average velocity or velocity, meters/second
Z	Electrokinetic potential, volts

<u>Symbol</u>	<u>Description</u>
ρ	Density kilograms/meter ³
τ	Relaxation time constant defined as $\epsilon\epsilon_0/k$, seconds

Prefixes

p	Pico, 10^{-12} x unit
n	nano, 10^{-9} x unit
μ	micro, 10^{-6} x unit
m	milli 10^{-3} x unit
k	kilo, 10^3 x unit
M	meg 10^6 x unit

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I. Introduction

Background

The accumulation of electrostatic charge in the handling of hydrocarbons has long been recognized in the Air Force and petroleum industry as a potential hazard. The current use of higher transfer rates created by the increased fuel capacity of the new large transport aircraft, and the extensive use of more volatile fuels is intensifying the hazard. In addition, fuel quality standards for the new generation of aircraft power plants requires cleaner fuel, that is, with smaller percentage of particulate contamination and dispersed water. Since most systems are low capacity and use steel piping and components, the above operational changes necessitates redesign of both fixed and mobile dispensing systems to allow use of corrosion free materials such as fiberglass or less reactive materials, such as aluminum or stainless steel. Since the majority of the refueling systems were built using schedule 80 steel pipe and mild steel fittings, most data related to static electric charge accumulation were based on relative motion between fuels and these materials. Little or no data are available for non metallic materials other than glass and only small quantities for non-ferrous metals.

Although the bonding and grounding phase of static protection is well under control, there still remains one area where static-ignition possibilities are not always recognized, or if known, are not practically avoided. This area involves those static-caused incidents that occur within tanks where vapor space exists above a free liquid surface. It is in this vapor space where the use of JP-4 has created the potentially more hazardous condition. JP-4, being a mixture of octane and aviation kerosine, has a vapor pressure specification with a minimum of 2 and a maximum of 3 psi Reid. In this pressure range, flammable mixtures could be encountered in a range of product temperatures extending as low as -20°C and as high as 30°C (Ref 2). This range would include most commonly encountered operating temperatures.

Between 1950 and 1960 the greatest amount of research was accomplished which considered static electricity in petroleum products. It is estimated that more than 150 technical papers and industrial reports were published in this time frame, but by far the most comprehensive is the work of Klinkenberg and Vander Minne (Ref 3). This report provides detailed theoretical and experimental considerations plus description of and reference to most of the important works previously accomplished by other researchers.

Review of the many technical reports and available data indicates at least one significant problem. There is a definite lack of correlation between data taken under reasonably similar conditions but at different times. This is not

difficult to understand, however, in that a large number of variables contribute to the electrostatic charging mechanisms, but only a very few can be directly controlled. Probably most important is the fact that many commercial hydrocarbon fuels are mechanical mixtures, and cannot be considered molecularly homogeneous or chemically identical batch to batch and from one time to another.

Objectives

The fact that previous investigations showed a wide range in most parameters associated with static electric phenomenon suggested that a study be made to investigate the appropriateness of previously developed theory to produce a single characteristic parameter which describes electrostatic activity. This physical parameter would be analogous, for instance, to solubility since it would describe a rate of activity between the hydrocarbon and another substance, namely the pipe. This would be similar to the relationship between solvent and solute even to the extent that the magnitude of the rate would be effected by other physical conditions such as temperature.

To this end, the following objectives were established:

1. The development of a parameter based on the theories of Helmholtz and Schon most recently reported by Hampel and Luther (Ref 4) which could.

a. Relate the rate of electrostatic charge production created by motion between various liquid hydrocarbons and solids.

b. Be defined at a standard temperature, pressure and safe current density.

2. The design and construction of experimental apparatus capable of establishing and verifying the magnitude of the parameter. The following operational conditions must be provided.

a. Current measuring capability in the range 10^{-6} to 10^{-16} amperes

b. Compatable insulation and shielding so that outside interference, noise and leakage is minimal

c. Independently measured parameters must be compatible, reproducible and of such degree of accuracy so as to preserve the overall accuracy

d. Apparatus and procedure must emphasize simplicity and a reasonably short recycle time

3. Gather data and compare experimental results with theoretical to the extent that:

a. The workability of the systems is demonstrated.
b. Data calculated, using the parameter, will compare at least to within an order of magnitude with experimental data.

Units

To preclude the confusion which arises from the use of mixed unit systems, especially where mechanical system interface with electrostatic systems, the rationalized metric system will be adopted throughout this report. The fundamental

quantities are length, mass, time, temperature and an electric quantity. Their units are meter, kilogram, second, degree Kelvin, and absolute ampere, respectively. Table I provides a list of derived quantities with their units. It should be noted that the volt is defined as a basic unit.

Table I

Basic and Derived Units

Quantity	Unit	Units Expressed in
Force	Newton (N)	kg m/sec^2
Energy, Work	Joule (J)	$\text{kg m}^2/\text{sec}^2$
Power	Watt (W)	$\text{kg m}^2/\text{sec}^2$
Potential	Volt (V)	$\text{kg m}^2/\text{sec}^2 \text{A}$
Resistance	Ohm (Ω)	$\text{kg m}^2/\text{sec}^3 \text{A}^2$
Charge	Coulomb (C)	A sec
Capacity	Farad (F)	$\text{sec}^4 \text{A}^2/\text{kg m}^2$

II. Theory

Charge Separation and Streaming Current

There is no general theory which totally describes the mechanism of electrification of hydrocarbon fuels. Hydrocarbon fuels can collect electric charges when flowing past a solid, for instance through a pipe, or when finely divided particles of a second substance, such as water droplets, settles through the fuel. These electrical phenomenon, caused by the relative movement between two phases, are known as electrokinetic phenomena in colloid chemistry. Most of the theories and mechanisms proposed for the electrification of hydrocarbons were an outgrowth of this science. In that most of these theories are for highly conductive aqueous solutions, their application to low conductivity hydrocarbons is very limited and questionable. For this reason, the parameter proposed in this study will be developed using only those theories of charge separation which have gained wider acceptance. Even under these circumstances, the variations found in most data related to electrification of hydrocarbons leads to a heavy dependence on experimental determination and verification of any factor.

Following the classical, Helmholtz, double-layer, theory, it is assumed that some ionized material in the hydrocarbon is selectively adsorbed at the fuel-solid interface. This ion transfer establishes a double-layer of charge of opposite sign with one layer of charge on the surface and the other

layer at a very small distance within the liquid. The potential difference at the double-layer seldom exceeds one volt and is normally between 0.01 and 0.1 volt (Ref 3 and 6). Relative movement at this interface will cause the two layers of charge to be separated.

When a hydrocarbon flows through a pipeline ions (negative by convention) attached to the pipe will tend to remain while the corresponding positive ions in the hydrocarbon will be carried with the flow. Thus, the negative ions which were previously bound in place by the proximity of the positive ions are now left free to flow to ground. Since some researchers make reference to probable chemical reaction, similar to electrolysis, at the interface it is reasonable to believe that the actual ion does not flow to ground but rather an electron exchange takes place and the electron flows to ground. As long as the fluid flows this is a continuous process of charge separation; positive charges carried downstream by the liquid while negative charges flow from the container to ground.

The actual amount of charge separation depends on the pipe material and surface condition, the hydrocarbon and type of ions, the pipe diameter and length and finally the average fluid velocity. The maximum charge density reached is limited by recombination of charges. Mutual repulsion of positive ions cause them to separate with some reaching the pipe wall. The recombination and repulsion separation mechanisms were described in the theory of transport of

electricity by diffusion published by Gorey and Chapman (Ref 5).

From the qualitative considerations above, Schon (Ref 4) calculated the influence of pipe length on charge density by evaluating the current flowing in and out of a differential volume element of length $d\ell$ in round pipe of radius R. The balance of incoming and outgoing currents is

$$di = 2\pi R(j_a - j_w)d\ell \quad (1)$$

where j_a is the current density issuing from the wall of the pipe and is considered the charging current. The current density of the charge leaking back to the pipe wall is j_w which is a function of the relaxation time constant τ and the total charge Δq contained in the volume $\pi R^2 d\ell$. So

$$j_w = \frac{i_w}{A_w} = \frac{\Delta q}{2\tau\pi R d\ell} = \frac{k}{ee_0} \frac{\Delta q}{2\pi R d\ell} \quad (2)$$

$$i = 2\pi R j_a d\ell - \frac{k}{ee_0} \Delta q = \frac{d\Delta q}{dt} \quad (3)$$

Streaming current, which is defined as the flow of electricity caused by the entrainment of charge by a flowing fluid, can be equated to $2\pi R j_a d\ell$ for the case where there is no relaxation. The finite charge Δq is contained in the volume $\pi R^2 d\ell$ but also moves with the fluid velocity \bar{V} . Then Δq must also be a function of the streaming current, namely, the product of i_s with a time $d\ell/\bar{V}$. This is all based on the fact that prior to any charge separation each separate charge

was mated with one of opposite sign.

Derivation of the Electrification Parameter, k_e

Using these facts, a relationship was derived for the current i_s based on the classical theory as modified by Cooper (Ref 6).

The Helmholtz equation for streaming current (Ref 3 and 6) is

$$i_s = \frac{-2\pi RT_{ss}ee_0Z}{n} \quad (4)$$

Knowing that Fanning friction factor is defined as

$$f \equiv \frac{\frac{T_{ss}}{\rho V^2}}{\frac{2}{R}} \quad (5)$$

and Reynolds Number as

$$R_e \equiv \frac{2\rho V R}{n} \quad (6)$$

Then substituting Eq (5) and (6) into Eq (4)

$$i_s = -\frac{\pi}{2} f R_e \bar{V} e e_0 Z \quad (7)$$

If this derivation is restricted to turbulent flow ($R_e > 3000$) which is not unreasonably restrictive when one considers operational systems, then f is known as a function of R_e and pipe roughness. The friction factor, f , may be obtained from a plot of R_e vs. f (Ref 3 or 9), or by calculation using the equation of Blasius:

$$f = 0.079 R_e^{-0.25} \quad (8)$$

which is for turbulent flow in smooth round pipes. Then Eq (7) becomes

$$i_s = \frac{0.079\pi}{2} R_e^{0.75} \bar{V} e_e Z \quad (9)$$

or

$$i_s = \left[\frac{0.0395\pi e_e Z \rho^{0.75}}{n^{0.75}} \right] D^{0.75} \bar{V}^{1.75} \quad (10)$$

Define

$$K_e \equiv \frac{0.0395\pi e_e Z \rho^{0.75}}{n^{0.75}} \quad (11)$$

which will be called the electrification parameter. If the electrokinetic potential Z could be readily obtained either empirically or theoretically, K_e could be computed and used in design. Since this is not possible and the variables describing the physical properties are all sensitive to temperature, an indirect experimental method is required to evaluate K_e .

Using the basic relationships just developed, an equation can now be tailored and written for a physical model. The capability exists for measuring current, potential, velocity and length by direct means. As a model consider an electrically isolated length of pipe with a hydrocarbon fuel flowing through it from a source tank to a receiver vessel. The

liquid motion relative to the walls was restricted to the electrically isolated test line. Therefore, the current I_p flowing to this line represents the net additional current caused by charge separation and diminished by charge relaxation. The time rate of change of charge on the slug of fuel, $\Delta\ell$ in length, is given by Eq (3). So that Eqs (3) and (10) may be combined, each must be put in terms of charge per unit length. The resulting differential equation applying to the slug of fuel moving at velocity, \bar{v} , is then

$$\frac{d \left[\frac{\Delta q}{\Delta \ell} \right]}{dt} = K_e D^{0.75} \bar{v}^{0.75} - \frac{1}{\tau} \left[\frac{\Delta q}{\Delta \ell} \right] \quad (12)$$

where

$$\tau = \frac{ee_0}{k}$$

A derivation of the relaxation time constant τ is provided at the end of this development. If an initial condition of $\Delta q = \Delta q_0$ when $\ell = 0$ and $t = 0$ the solution of Eq (12) is

$$\frac{\Delta q}{\Delta \ell} = \frac{\Delta q_0}{\Delta \ell} + \left(\tau K_e D^{0.75} \bar{v}^{0.75} - \frac{\Delta q_0}{\Delta \ell} \right) \left(1 - e_n^{-t/\tau} \right) \quad (13)$$

Since $\ell = \bar{v}t$, in terms of length Eq (13) becomes

$$\frac{\Delta q}{\Delta \ell} = \frac{\Delta q_0}{\Delta \ell} + \left(\tau K_e D^{0.75} \bar{v}^{0.75} - \frac{\Delta q_0}{\Delta \ell} \right) \left(1 - e_n^{-1/\tau \bar{v}} \right) \quad (14)$$

If we assume each slug of fluid undergoes the same charging, the current flow into the pipe from the source container is:

$$-I_s = \left(\frac{dq}{dt} \right)_{\ell=0} \left(\frac{d\ell}{dt} \right) = \left(\frac{\Delta q}{\Delta \ell} \right)_{\ell=0} = \bar{V} \left(\frac{\Delta q_0}{\Delta \ell} \right) \quad (15)$$

where I_s is defined as the current flowing from the source container to the ground. I_R is defined as the current flowing from the receiving vessel to ground. At $\ell = L$ the current flowing from the pipe to the receiver is

$$I_R = \bar{V} \left(\frac{\Delta q}{\Delta \ell} \right)_{\ell=L} = -I_s + (\tau K_e D^{0.75} \bar{V}^{1.75} + I_s) (1 - e_n^{-L/\tau \bar{V}}) \quad (16)$$

Now if one considers the currents after steady state is reached, then the sum of the three currents will be zero or as stated previously the charges appear in matched pairs of opposite sign. From Eq (14), (15), and (16) the current flowing from the pipe to ground is determined as

$$I_p = -I_s - I_R = -(\tau K_e D^{0.75} \bar{V}^{1.75} + I_s)(1 - e_n^{-L/\tau \bar{V}}) \quad (17)$$

All variables in Eq (17) except K_e are easily obtained experimentally. The time constant τ , however, is normally obtained from an independent experimental determination of conductivity.

The electrification parameter K_e only provides an indication of the charge buildup which can be expected. In a similar way the time constant τ is related only to the

charge dissipation by relaxation. To obtain a parameter which better indicates the overall electrification process the product τK_e will be used.

Then from Eq (17)

$$\tau K_e = \frac{-I_p - I_s (1 - e_n^{-L/\tau V})}{D^{0.75} V^{1.75} (1 - e_n^{-L/\tau V})} \quad (18)$$

Charge Relaxation

The concepts of relaxation time and half value time were first put forward by Warburg in connection with a paper by Holde (Ref 3). They are applied to the electrokinetics of hydrocarbon fuels in the identical manner as they are in the calculation of the characteristics of capacitors. The following short derivation of the relaxation time τ should indicate the significance of the concept. In a charged capacitor with a dielectric which is conductive, the leakage current i can be expressed as

$$i = \frac{dQ}{dt} = \frac{V}{r} \quad (19)$$

where r is the total resistance and V the potential between the plates. From the definition of capacitance the potential across the plates

$$V = \frac{Q}{C} = \frac{Q\ell}{\epsilon_0 A} \quad (20)$$

From the definition of resistance, resistivity and conductivity

$$r = \frac{\rho \ell}{A} \quad (21)$$

or since $r^* = 1/k$ where k is conductivity

$$r = \frac{2}{Ak} \quad (22)$$

Substituting Eq (20) and (21) into Eq (19)

$$\frac{dQ}{dt} = \frac{kQ}{\epsilon\epsilon_0} \quad (23)$$

which yields

$$Q = Q_0 e_n^{-kt/\epsilon\epsilon_0} \quad (24)$$

The time constant or relaxation time is

$$\tau = \frac{\epsilon\epsilon_0}{k} \quad (25)$$

The half value time t' is the time required for the charge of a capacitor to be reduced from Q_0 to $Q_0/2$. Thus

$$e_n^{-t'/\tau} = 1/2$$

or

$$t'/\tau = \ln 2 = 0.693 \quad (27)$$

In the hydrocarbon fuels the relaxation time varies widely from a few milliseconds for crude oils to many minutes for highly refined waxes. Since the magnitude of the relative dielectric constants ϵ of the hydrocarbons of interest is always approximately 2.0 the major variation can be attributed to the conductivity. This can be easily shown by the fact that conductivities will vary from the greatest to

the least by a factor of approximately 10^8 .

The theoretical concepts discussed herein provide the basis for this experimental investigation. Many other theories contribute to this work but only to a lesser degree. For these, derivations are not provided, however, they are readily available in the literature referenced.

III. Experimental Apparatus

There were three major pieces of apparatus used in conducting this investigation. Each of these can be further subdivided into as many as five major component groups. This equipment was the conductivity cell with its power supply and instrumentation; the gravity flow charging tendency device with its inert gas atmosphere, shielding, and instrumentation, and finally the pipe flow equipment with its pressurizing system, temperature monitoring equipment, instrumentation, shielding and inert gas atmosphere. Schematic diagrams of the apparatus including sectional views of the non-standard equipment are provided in Appendix A.

Conductivity Cell

Figure 1 shows a sectional view of the conductivity cell. The basic block diagram of the components of the apparatus, including an insert showing the wiring schematic of the constant voltage source, is given in Fig. 2.

A parallel plate capacitor is the main part of the conductivity cell. One electrode of the capacitor is set on a good insulator (resistivity of 10^{13} ohms centimeters or better) and can be connected to a constant voltage source. The second electrode is electrically insulated from all other parts of the cell by the best available insulating material (resistivity 10^{18} ohm centimeters or better). This is the one which collects the charge and which is connected directly

to the electrometer. Teflon, having resistivity greater than 5×10^{21} ohms centimeters, was used to construct both electrode insulators. A grounded guard ring surrounds the collector electrode which shields it from stray currents. A glass sample holder is provided whose volume is in excess of 150 milliliters. The electrode connected to the voltage source is mounted perpendicular to the axis of symmetry of the sample holder. As shown in Fig. 1 this entire assembly is mounted on a precision screw which permits the distance between the electrodes to be continuously adjustable from 0 to 25 millimeters while being maintained parallel. The diameter of the sample container is sized so that the collector electrode and the guard ring fit inside and can be submerged in the sample. The method of fastening used throughout the assembly provides rigidity and prevents changes in the cell's characteristics caused by vibrations.

Several special features were designed into the cell. First a dial gauge was added so that the distance between the electrodes can be measured to within 0.01 of a millimeter. The electrodes were plated with a minimum of .005 inches of silver. This was done so that cleaning would be relatively easy and the surfaces would be inert to all hydrocarbons. The outer container for the assembly is made of stainless steel and serves primarily as an electrical shield and direct connection to the electrometer preamplifier case. With very minor modifications the shell could be pressurized with dry, inert gas so as to reduce current leakage through the

atmosphere if very low current measurements are required.

The constant voltage source is provided by good quality batteries. A 22.5 volt multiple output battery, commonly used in electronic equipment, was encased in an aluminum chassis box for this purpose. The output voltages obtainable are based on the battery taps but a three volt bias may be used if a particular experimental voltage is desired.

One electrometer used to measure the current flowing through the cell is a vibrating reed type capable of measuring currents between 1.0×10^{-12} and 1.0×10^{-17} amperes originating in a high impedance source. Since the currents to be measured in this study were all above 10^{-15} amperes a calibrated high value resistor was used to measure the currents by the steady deflection method.

The other electrometer used is an electronic type with current measuring capability in the range of 0.1 picoamperes up to 1 milliampere. The meter, although not as sensitive, is battery operated and has the advantage of being isolated from line voltage fluctuations and transients.

During calibration of the conductivity cell two methods were used which required separate circuitry and instrumentation. Appendix C describes the required apparatus along with the calibration procedure.

Gravity Flow Charging Tendency Device

Figure 3 is a schematic diagram of the apparatus which includes critical dimensions, instrumentation, and shielded

enclosure with inert atmosphere. The dimensions established are only critical in that an attempt was made to duplicate the equipment and procedure used by Royal Dutch Petroleum Company (Ref 5). The apparatus consists of SAE 4304 stainless steel alloy tubes (inside diameter 2.18 mm) which can be connected interchangeably to a container of the same alloy. This container has a volume in excess of three liters and a simple valve in the bottom to start and stop the flow. The tube connection is made so that the entrance is flush with the bottom of the container. The liquid to be tested is allowed to flow under the influence of gravity from the upper container to a similar lower container.

The three components just discussed are assembled as shown in Fig. 5. The receiver vessel is insulated from ground by blocks of styrofoam and teflon while the stainless steel tube and source vessel is grounded either directly or through a picoammeter. The receiver vessel is connected by coaxial cable to an electrometer which is used in an electrostatic voltmeter mode. During tests, this meter was used interchangeably with a standard electrostatic voltmeter with a relaxation time greater than 10 minutes and a range of 150 volts. To maintain the potential between the receiver and stainless steel tube below 10 volts the receiver was shunted to ground through a capacitor. The shunting capacitor used had low leakage and was calibrated. A General Radio Corporation variable precision capacitor with a range of 11 to 1120 picofarads was used. The shunting resistor was a

Victoreen Corporation "HiMeg" with a resistance of 100,000 megohms, and good thermal and current variational stability.

During the test the apparatus is enclosed in a metal clad box which acts both as electrical shielding and a container for the inert atmosphere.

Loose equipment included a stopwatch and sling psychrometer. Respectively, these were used to determine the time required for 1 liter of sample to flow from the upper container to the receiver, and to obtain an indication of the effectiveness of the inert gas drier to maintain the humidity below 10%.

Apparatus for Determining Static Charging in Full Pipelines

The test setup used for the experiment is shown in Fig. 4. The flow of the sample hydrocarbon through the stainless steel tube is caused by a differential pressure created by varying the height of the mercury columns. The pistons on each end of the sample fluid maintains a closed system with no liquid or vapor losses. Teflon insulation material is used as shown for electrical isolation between sections of the equipment and between the equipment and ground. In addition, the entire system is electrically shielded in a metal clad box and surrounded by an inert atmosphere of clean, dry, nitrogen.

The apparatus is divided in three sections each of which is electrically isolated from the others. The source and receiving vessels are identical in design. Each is a SAE 4304

stainless steel alloy cylinder with a 133.1 millimeter bore fitted with a piston. The maximum piston travel is 44.5 millimeters which corresponds to 620 milliliters fluid displacement.

Assuming incompressible flow through the test pipe which has a cross sectional area of 3.75 square millimeters, a velocity range of 1 to 33 meters per second may be obtained in a 5 to 165 second time interval. The position of the piston, its stroke length, and time of traverse were recorded on a Visicorder using a linear potentiometer pickup connected by suitable mechanical linkage.

Referring again to Fig. 4 it is noted that each section is connected to ground through a sensitive picoammeter. These meters measure the current flowing to or from ground from each section. A more complete description of the transfer of charge and the direction of current flow will be given during the discussion of procedure.

An additional configuration of the apparatus was used to determine rise in temperature of the fluid as energy was applied in the form of the pump work. Five calibrated copper-constantan thermocouples were placed at critical points in the system as shown in Fig. 5. The temperatures were recorded on a multipoint potentiometer type recorder using a standard thermocouple circuit. The extension wires between the junctions and the recorder were thermocouple grade copper. The system accuracy was well within the $\pm 1.5^{\circ}\text{C}$ required.

IV. Experimental Procedure

The investigative procedure involved two primary tests and several supporting experiments. As a prerequisite to understanding the test procedure the quantities to be measured and how they will be used must be determined. For a pipe and hydrocarbon fuel combination the length and diameter of the pipe will have to be known. The variables to be determined will be velocity \bar{V} , relaxation time constant τ , current flowing from source vessel to ground I_s , current flowing from the pipe to ground I_p , the inside diameter of the tubing D , and the tube length L .

Conductivity and Relaxation Time

First consider the use of the conductivity cell to determine k and the dielectric constant which were used to calculate τ .

The apparatus is prepared and cleaned as described in Appendix D and then connected to the other equipment as shown in the schematic of Fig. 6. Next the cell was calibrated, using a modification of the proposed ASTM method (Ref 7). This is described in Appendix C, Operating Procedure and Equipment Calibration.

Even though there are two methods available to measure conductivity (Ref 3) the proposed ASTM method (Ref 7) was used with minor modifications. This utilizes what is considered the direct method and is applicable in the same resistance range as Ohm's law. A vibrating reed electrometer

connected in series with the cell measures the current flowing through the sample liquid which is acting as the dielectric in the parallel plate capacitor. The constant voltage supply maintains a potential between the electrodes of the cell. Prior to each test this potential is measured with a high internal impedance voltmeter or an electrometer using a calibrated resistor. After calibration and standardization is completed and the cell constant K_c has been calculated the circuit is reconfigured as shown in Fig. 2.

The equipment is now ready for conductivity measurements. Once the cell has been placed into service the initial cleaning process may be omitted, but the final cleaning process is still required. See Appendix D for details. The cell is reassembled and leveled making certain the distance between electrodes is not changed from that used in calibration. By this time the instrumentation should be completely warmed up and all signals stabilized so that the test may proceed. The liquid to be investigated is poured into the sample container through the access left by not replacing the collector electrode during reassembly. To obtain reproducible results the electrodes must be submerged approximately the same amount for each test. This requires that the fluid level in the sample container be maintained within ± 1 millimeter measured from a point located on the collector electrode. To accomplish this, the test liquid was poured into the cell until the free surface coincided with the lower surface of the guard ring. A measured volume of sample of

between 3 and 5 milliliters was then added to get the proper electrode coverage. It was found that reproducible results could be obtained anywhere within this range using the previously described instrumentation sensitivity.

The remaining part of the cell are assembled and the required potential range calculated using

$$V_{\max} = 1.5 l \quad (28)$$

and

$$V_{\min} = 0.8 l \quad (29)$$

where l is the electrode separation in millimeters (Ref 3 and 7).

The open circuit voltage of the battery power supply is measured and recorded after the range of potential is selected but prior to connection to the cell.

The potential is then applied across the cell electrodes after making certain the voltmeter is no longer in the circuit. The current which flows through the cell is measured by the electrometer making use of the best scale. The magnitude of the peak current, which occurs immediately after the voltage is applied, is the value used to compute conductivity. Because of this, it is desirable to record the current as a function of time so that the exact peak can be determined.

The conductivity κ is then calculated from the measured current i , voltage V , and the cell constant K_c .

$$k = \frac{K_c i}{V} \times 10^{12} \quad (30)$$

where k has the units of picohm/meter when the current i is in amperes, V in volts, and K_c is in centimeters $^{-1}$.

By using a precision A.C. bridge and the calibrated cell where K_c the cell constant is known, the relative dielectric constant can be measured. Then by using Eq (25) the relaxation time constant can be calculated.

Electrostatic Charge Separation

Once the relaxation time constant has been calculated the problem is to determine the velocity of the hydrocarbon fuel through various length pipes experimentally and the resulting electrostatic charge separation. The apparatus shown in Fig. 4 and described in the previous chapter is used after being cleaned and prepared as described in Appendix D. The test procedure consists of measuring the current from each of the three isolated sections to ground under various flow rates and tube lengths.

After cleaning and installing a tube of a particular length, the system is filled with the sample liquid making sure no air is trapped in the vessels or line. During the process, the maximum travel of the pistons must be established. Initially all that is required is to insure that sufficient travel is available. Then the accurate travel distance is measured with a micrometer, depth gauge and the stops set. With this accomplished and the desired fluid velocities

selected the differential pressures required are calculated. This is done by assuming incompressible flow and no pressure loss due to pipe friction, calculating the required pressure differential in inches of mercury and adding 33 inches which is the pressure differential required to overcome static frictional resistance of both pistons. Since the sample was in motion during the filling operation and could be changed, a relaxation period of at least thirty minutes is allowed. During this period all three components are interconnected with a grounded wire. Prior to beginning the actual test the interconnection is removed from each component while remaining connected to ground. This is done so that change is not transferred from the operator to the equipment.

The required pressure is now set by adjusting the height of the mercury reservoirs until the manometer indicates the calculated number of inches of mercury differential. During this adjustment the flow of mercury to the apparatus is prevented by a clamp on both connecting tubes.

An initial reading of each current is taken while the test fluid is at rest. All should read zero. Then with the meters in the "read mode" the recorder is started and the hose clamps are released. As the fluid begins to flow the charge separation in the pipe will cause a current, I_p to be indicated on one meter. The meter in series with the source vessel's ground which would read the current I_s will indicate zero as long as care is taken to insure the sample liquid is initially fully discharged or at such low level as to be

negligible. The meter in series with the receiving vessel ground initially will indicate a current opposite in direction and lagging in magnitude to I_p .

After approximately three seconds the currents should stabilize with their sum equal to zero within experimental accuracy. The time required to determine the velocity is obtained from the recorder on which the abrupt change in slope of the trace indicates the beginning and end of the piston travel.

To obtain data at different velocities, the procedure is repeated after changing the differential pressure. For this investigation velocities of approximately 1, 3, 6, and 9 meters per second was used. After gathering the data for these velocities the length of tubing was increased and the whole procedure repeated. The tubing lengths used were 0.20, 0.50, 1.0 and 1.5 meters, which constituted a complete sequence for that particular hydrocarbon sample. The diameter was held constant at 2.18 millimeters. To continue the test a cleaning cycle must be accomplished prior to introducing a different sample liquid and going through the total procedure again.

Environmental Precautions

In addition to these procedures, environmental controls were required. They included a dry nitrogen atmosphere around the apparatus and electrostatic shielding. Both of these requirements were described previously. The relative humidity

of the nitrogen atmosphere was estimated initially but later discontinued. The action was taken after it was found that the relative humidity of the nitrogen was on the order of 5% as delivered from the drier and that the apparatus and container made no significant contribution to the moisture. As long as a positive pressure of between 1 and 3 inches of water was maintained after the ambient air was flushed out by an initial 10 minute high volume flow, the relative humidity was well below the values published by other researchers (Ref 3) as being satisfactory.

Electrostatic Charging Tendency

The gravity flow apparatus for the determination of electrostatic charging tendency was used as a screening experiment in this investigation. Its total purpose was to insure that the hydrocarbon being tested in the primary apparatus would, in fact, generate a static electric charge. Since the detailed procedure for the use of this apparatus was published by Klenkenberg (Ref 3) a condensed version with the local modifications is provided in Appendix C.

Temperature Rise Determination

An experiment was conducted to determine the temperature rise in the hydrocarbon fuel caused by the energy input used to create the flow. The procedure was identical to that used for measuring charge separation during full pipe flow except in lieu of measuring the three currents, five thermocouples were installed to measure the fluid temperature. The tempera-

ture rise was determined using the highest velocity condition (greatest energy input) with each of the four lengths of tubing. The temperatures were recorded by a Honeywell multipoint recorder both while the fluid was flowing and for 5 to 10 minutes after flow stopped.

Chemical Analysis

Qualitative and quantitative chemical analysis of the hydrocarbon samples are not required for the success of this investigation. Since follow-on studies would require this information for the purpose of data comparison, a basic analysis was obtained from an independent laboratory source. Their entire report will be maintained in the records of this experiment for future use.

V. Results and Discussion

The theoretical development of a comparison parameter τ_{K_e} which is based on experimentally measurable, physical, properties has been accomplished. In order to estimate the value of this parameter, experimental apparatus and operating procedures had to be designed and tested. This project entailed the development and construction of the three pieces of apparatus described previously. Data which can be obtained from each of these pieces of equipment will be discussed relative to their accuracy and repeatability. Along with this, the equipment and procedure will be evaluated and potential improvements indicated where applicable. Each piece of equipment will be discussed individually followed by an evaluation of the preliminary data.

The Measurement of Conductivity

The electrical resistivity or its reciprocal, conductivity, determines the rate at which accumulated charge will relax or dissipate from a hydrocarbon. For this reason accurate, repeatable values of conductivity are required to insure consistency in the developed comparison parameter over a wide range of hydrocarbon-solid interfaces.

Many experimental difficulties arose when measuring the low conductivity of hydrocarbon fuels. These can be established in two groups namely those relating to the measurement itself and those caused by adsorption. A third problem is the change in conductivity with time which is normally a

decrease. This change is ascribed to the colloidal character of many solutions and impurities in hydrocarbons and thus internal equilibrium proceeding very slowly. In addition, the chemical and physical properties of many hydrocarbons change with time through the evaporation of the lighter fractions and absorption of gases and substances such as water.

The equipment design and procedure used were established to minimize these effects whenever practical. Other difficulties such as the ionization caused by cosmic radiation could not be compensated, so their effects had to be recognized and treated accordingly.

Polarization, associated with the passage of direct current through an electrolyte, causes a decrease in conductivity with time. The factors which contributes to this include the low rate of reaction at the electrodes, concentration changes in the fluid near the electrodes and the accumulation of electrolysis products on the electrodes. Since it can be proven that direct current must be used in conductivity measurements in hydrocarbons (Ref. 3), two methods of minimizing these effects were included. First the field strength was kept as low as possible (between 800 and 1500 volts/meter) and second, the current was measured at a time as close as practical to the time of potential application. These procedures are recommended by most researchers (Ref 3 and 4).

Adsorption, which removes the very small concentrations of ion impurities which contribute to the conductivity, was

limited by rinsing all wetted parts with the liquid being investigated (see Appendix D). In this way adsorption equilibrium is reached prior to introducing the sample on which the test is performed.

The required electrical characteristics of the cell and the current measuring techniques demanded special design consideration to minimize potential errors. For example, the distribution of the electric field in the chamber must be accurately defined. Therefore, the parallel plate electrode configuration was selected since it provides excellent field definition. Other advantages are the ease of construction and guarding against stray currents, and simple geometry useful in the calculation of cell capacitance or constant.

The problem of static electric charging is most critical in a relatively small range of conductivities approximately 10^{-9} to 10^{-14} picombohm/meter (Ref 3). Hydrocarbons with conductivity above this range have short time constants and, therefore, relax at such a high rate that significant charge is not built up. If the conductivity of the fluid is very low, below 10^{-14} ohms/meter the rate of charge separation is small and adsorption and interface effects tend to maintain it close to a neutral equilibrium. For this reason the range of the current measuring equipment was selected between 10^{-9} and 10^{-15} amperes.

The electrometer and micro-micro ammeter used in the conductivity measurements are primary sources of error. First the vibrating reed electrometer is not an absolute

instrument so calibration against known values is essential. Techniques recommended by the equipment manufacturer were used for calibration and to determine the quality of performance. To maintain reproducibility and accurate calibration required constant care to insure insulators were not stressed, temperature fluctuations within the equipment were minimal, and the circuit configuration were not changed.

The sensitivity of the equipment in the 10^{-14} to 10^{-16} amperes range is such that stress in insulating materials and changes in temperature cause extreme electronic noise problems. These problems are temporary and will disappear in about 24 hours if the temperature is allowed to stabilize and stresses allowed to relax.

After gaining some experience with the equipment problems such as those described could be avoided. Other noise problems such as those associated with the ionization effects of radiation were not significant in this investigation. The magnitudes of the conductivities measured were large enough so that these effects could be neglected.

A.S.T.M. (Ref 7) provides standards for repeatability and reproducibility of conductivity measurements which are a function of conductivity magnitude. To date the data collected and shown in Table II indicates these standards will be met. However, before a final determination can be made, more data must be collected and statistically analyzed. The rate of data acquisition is extremely slow since the cell cleaning procedure which consumes about 90% of the cycle time is excessively long.

Table II

Measured Conductivities¹

Product	Test Number	Conductivity picomho/meter
JP-4	11	5.70
	12	5.84
	13	5.55
	14	6.00
	15	5.83
	16	5.30
Hexane	21	0.380
	22	0.379
	23	0.380
	24	0.380
	25	0.360
	26	0.398
Carbon Tetrachloride ²	51	3×10^{-2}
	52	5×10^{-5}
Benzene ³	41	6.1×10^4
	42	7.2×10^4
Xylene	51	0.04

1. The conductivity of the samples was measured in a random order making certain that like samples were not measured one after the other.
2. Since the current was below 10^{-15} amperes the time rate of change of charge on the capacitor was used to measure this conductivity. This method without specific calibration is only approximate.
3. Measured using Kiehley Electrometer.

Cell Constant

The cell constant, determined by the direct method, was 0.0225 cm^{-1} . This value is based on 5 millimeters electrode separation. If other gap settings are used a new constant must be experimentally determined. The relationship between

the constant and the gap dimension is only approximately linear. The variation is produced by the inability to produce two electrode surfaces which are exactly parallel at all gap settings.

Hydrocarbon Charging Tendency

The gravity flow apparatus for determining charging tendency was only used as a screening experiment. The hydrocarbon to be investigated in the primary apparatus was tested in this equipment to insure that it did separate charge during flow. The JP-4 sample which had a conductivity of 5.84 picomho/meter the charging tendency varied from 40 to 70 micro coulombs/meter² depending on the length of tube and variation in velocity.

The equipment was calibrated by the procedure outlined in Appendix C. The capacitance of the lower vessel was 52 picofarads. The calibration was undertaken to permit a preliminary evaluation of the electrostatic charging occurring in the case with a free jet and in the full pipe flow without a free jet. Even though no attempt was made to establish a finite magnitude of the contribution of the free jet to the overall charging tendency it appeared to be significant. For instance, in the flow through the one meter tube, the velocity was approximately 1.2 meters/sec as determined from the time required for a one liter sample to flow to the lower container. Since the fluid wets the container and tube and the entire liter sample does not flow, the velocity is only

approximate but of sufficient accuracy for this investigation. Assuming the velocity is between 1.2 and 1.4 meters per second in gross figures, the charging tendency with the free jet was in excess of 20% higher than the case without the jet. The data in Table III shows the charging tendency calculated by the two methods. This provides a definite indication of the magnitude of the contribution of the free jet and is why the charging tendency derived from previous experiments is not representative of pipe flow or useful to designers.

Electrostatic Charge Separation

As explained in the development of the theory and the procedure, the current measurement obtained from the primary apparatus will be used to calculate the electrostatic charging parameter K_e and the comparison parameter τK_e . Since the time constant τ was determined independently, the only remaining unknown is K_e which is readily obtained by using Eq (18).

Before discussing this calculation, some features designed into the equipment should be explained. Most important of these is the piston to tube cross sectional area ratio. Considering a 5% accuracy in electrical measurements is possible after careful calibration, an area ratio was desired which would allow the velocity of the fluid to be neglected in the source cylinder when compared to that in the tube. In addition, the volume of fluid displaced had to be great enough to provide adequate time for making electrical measurements manually if necessary. The latter item controlled

Table III

Charging Tendency Calculated from Two Experimental Methods

pipe length meters	Velocity meters/second	Charging Tendency with free jet	Charging Tendency from full pipe flow	Percentage difference
		micro Coulombs/meter ³	micro Coulombs/meter ³	
1.0	1.2-1.4	54	43	26
1.5	1.2-1.4	73	60	22

the decision and an area ratio in excess of 5000:1 piston to tube was needed. Actual ratio attained was 3580:1.

The question of current flowing from one section of the equipment to the other through the insulation or through the fluid arises. In other apparatus, such as the one used in the screening experiment, this is important since total charge is being measured. In the pipe flow equipment, however, the steady state current flowing between each of the three sections and ground is measured. Current flowing between sections is determined by Ohm's law for the potential between sections. Since all three sections are connected through three meters to a common ground, the difference in resistance of the meters will determine the potential between sections. This potential is found to be zero within experimental accuracy.

The preliminary experimental data shown in Table IV, when analyzed, provides additional insight into what physically occurs. First, within experimental error, the sum of the three line currents is zero. It should be noted that the current was not measured between the source cylinder and ground after initially determining that with no initial charge on the fluid it had to be zero. Inasmuch as the net current flow to or from the test set up would indicate a change in potential of the entire system the current sum being zero can be expected. Table IV, Column 6 indicates that the actual data agrees with this within expected error.

Table IV

Current Generated by JP-4 Flowing in Stainless Steel Tubing¹

Length of Test Line Meters	Velocity Meters/ Second	Source Cylinder Pipe	Current 2				Current 2				Current 2			
			I_s	I_p	I_R	$I_s + I_p + I_R$	I_s	I_p	I_R	$I_s + I_p + I_R$	I_p	I_R	$I_s + I_p + I_R$	I_p
0.2	1.013	0	-	0.05	+ 0.04	0.01	-	.44	0.39	-	.44	0.39	-	.39
0.2	2.786	0	-	1.60	+ 1.80	0.20	-	.98	0.62	-	.98	0.62	-	.62
0.2	6.000	0	-	3.20	+ 3.90	0.70	-	1.72	1.48	-	1.72	1.48	-	1.48
0.2	9.750	0	-	1.20	+ 1.70	0.50	-	2.50	1.30	-	2.50	1.30	-	1.30
0.5	1.000	0	-	1.60	+ 1.90	0.30	-	1.05	0.55	-	1.05	0.55	-	0.55
0.5	2.889	0	-	3.20	+ 3.30	0.10	-	2.45	0.75	-	2.45	0.75	-	0.75
0.5	5.200	0	-	4.40	+ 4.10	0.30	-	3.85	0.55	-	3.85	0.55	-	0.55
0.5	8.667	0	-	7.00	+ 5.90	1.10	-	5.70	1.30	-	5.70	1.30	-	1.30
1.0	1.147	0	-	2.10	+ 2.00	0.10	-	2.20	0.10	-	2.20	0.10	-	0.10
1.0	2.690	0	-	4.60	+ 4.90	0.30	-	4.51	0.09	-	4.51	0.09	-	0.09
1.0	7.091	0	-	10.00	+ 10.40	0.40	-	9.66	0.34	-	9.66	0.34	-	0.34
1.0	13.000	0	-	15.30	+ 16.10	0.80	-	15.40	0.10	-	15.40	0.10	-	0.10
1.5	.987	0	-	3.00	+ 2.80	0.20	-	2.69	0.31	-	2.69	0.31	-	0.31
1.5	2.889	0	-	6.60	+ 6.60	0.00	-	6.97	0.37	-	6.97	0.37	-	0.37
1.5	5.200	0	-	11.20	+ 10.60	0.60	-	11.20	0.00	-	11.20	0.00	-	0.00
1.5	9.750	0	-	18.40	+ 17.70	0.70	-	18.40	0.00	-	18.40	0.00	-	0.00

¹ $\tau = 3.2$ seconds² currents are in units of 10^{-10} amperes

During the data acquisition several observations were made. First, in the short pipe lengths and at all velocities the current measurements did not reach a stable value. Initially, this appeared to be an instrumentation problem but later was ruled out since the longer tubes reached stability. The reason for this instability is found in theory. It was assumed that the flow was fully developed turbulent which probably never occurred in the short pipe. In addition, velocity gradients associated with entrance effects would be found for the entire length of the pipe. Both of these effects would influence the thickness of the boundary layer, the electrokinetic potential and rate of charge migration. This was also observed by other researchers and reported by Klenkenberg (Ref 3).

Another possible cause of instability is the fact that all data collected was for tubes below the critical length. The critical length is defined as $\tau\bar{V}$ and represents a length at which the sample would be in contact with the pipe for the duration of its relaxation time. This effect would cause errors in all measurements but be most pronounced in the shorter pipe lengths where the current generated by charge separation would be approximately the same order of magnitude as the error due to length. The graphs of pipe current as a function of length and velocity, Figs. 7 and 8 in Appendix B, show this greater deviation in the short pipes.

The effects just discussed along with the limited extent of preliminary data taken made it necessary to use an average

value of K_e based on the 1.5 meter tube length. Using this value of K_e the pipe current I_p was calculated using the velocity, time constant and length values in Table IV. This then is the origin of the computed curves shown in Figs. 7 and 8. Even with the limited data taken, which was felt sufficient to show the workability of the apparatus, agreement between the experimental and calculated values of I was found to be of the same order of magnitude as the data. Column 8 in Table IV provides the comparison as the magnitude of difference between I_p and I_p' .

From this comparison it is seen that a single value of the parameter τK_e appears valid for a wide range of velocities and pipe lengths. Thus, a single value of τK_e can be used to indicate the relative charging potential of a single combination of hydrocarbon fuel and container material.

IV. Conclusions and Recommendations

Conclusions

The conclusions listed below were reached as a result of this experimental investigation.

1. The parameter τK_e which is composed of the product of the electrification and relaxation time constants provides an indication of the combined effects of the charge buildup and reduction which occurs simultaneously.
2. The parameter τK_e when evaluated experimentally for various combinations of hydrocarbon fuels and container materials will indicate the relative magnitude association with each combination.
3. It is observed that for very long pipelines and negligible source current I_s Eq (17) could be expressed approximately as

$$I_p = - \tau K_e D^{0.75} \bar{V}^{1.75} \quad (31)$$

From this it can be seen that charge density does not continue to increase with length but reaches a limiting value proportional to the liquid velocity, pipe diameter and the parameter τK_e . This observation was not proven experimentally but does agree with the findings of other researchers (Ref 3).

4. Using the equation

$$I_p = - (\tau K_e D^{0.75} \bar{V}^{1.75} + I_s)(1 - e_n^{-L/\tau V}) \quad (32)$$

one observes that a good curve fit is obtained for a wide

range of velocities provided the pipe has sufficient length to allow the flow of both fluid and charge to stabilize.

5. Both the conductivity cell and the other apparatus function as predicted are capable of producing the required data.

6. The recycle time, which is dependent on the time required to clean the equipment, is too long and must be improved if a large number of tests are to be run.

Recommendations

1. The comparison parameter τK_e developed could be a valuable tool for systems designers. Further study should be undertaken to examine the parameter for different fluid-material combinations and also to establish standard conditions for its acquisition and application.

2. The basic design of the conductivity cell should be improved from the standpoint of ease in cleaning. In addition it should be made smaller, more compact and ultimately developed into a self contained piece of portable laboratory equipment. This would entail optimization of the component parts relative to their use rather than the ease of manufacture as was done in the original cell.

3. The magnitude of the issuing current obtained from this investigation using the pressurized pipe flow apparatus may be compared with the issuing current found from the gravity flow apparatus. The difference between these magnitudes is the charge buildup which occurs in the free jet.

An indepth study of the phenomena associated with this type of charging would be extremely beneficial. Its effects are presently being avoided at great design and construction expense mainly because a knowledge of the exact hazards are not available.

4. A redesign of the sample holder and lower electrode insulator should substantially reduce the cleaning problem. In lieu of six separate parts the two piece redesign shown as an insert in Fig. 1 is proposed. It utilizes a machined teflon or polyethylene sample container-insulator combination. The lower electrode uses a press fit, taper to both fasten and seal its edge. This design allows ready access by cleaning solvents to all surfaces which was not possible with first design.

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Appendix A

Apparatus Drawings and Schematic Diagrams

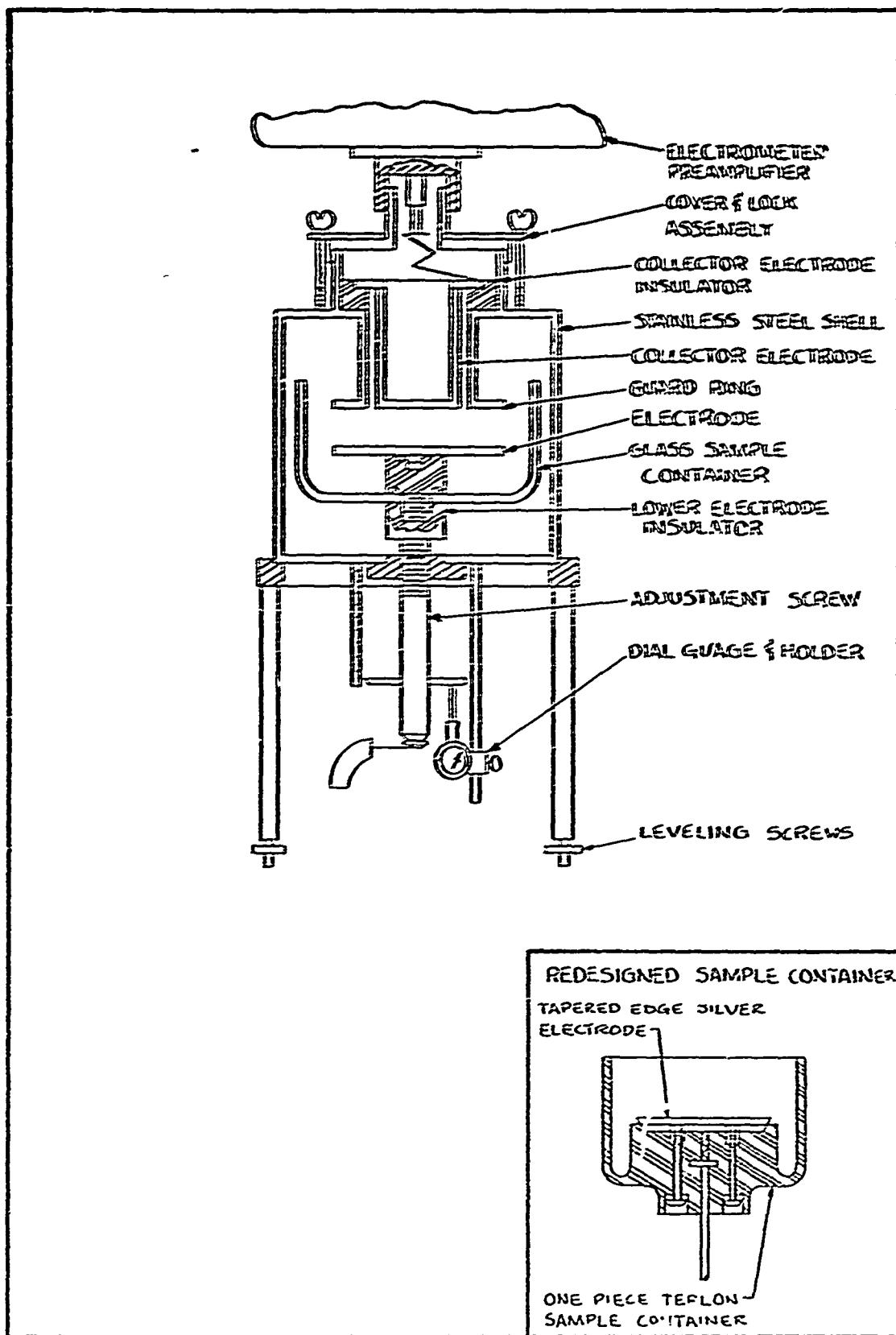
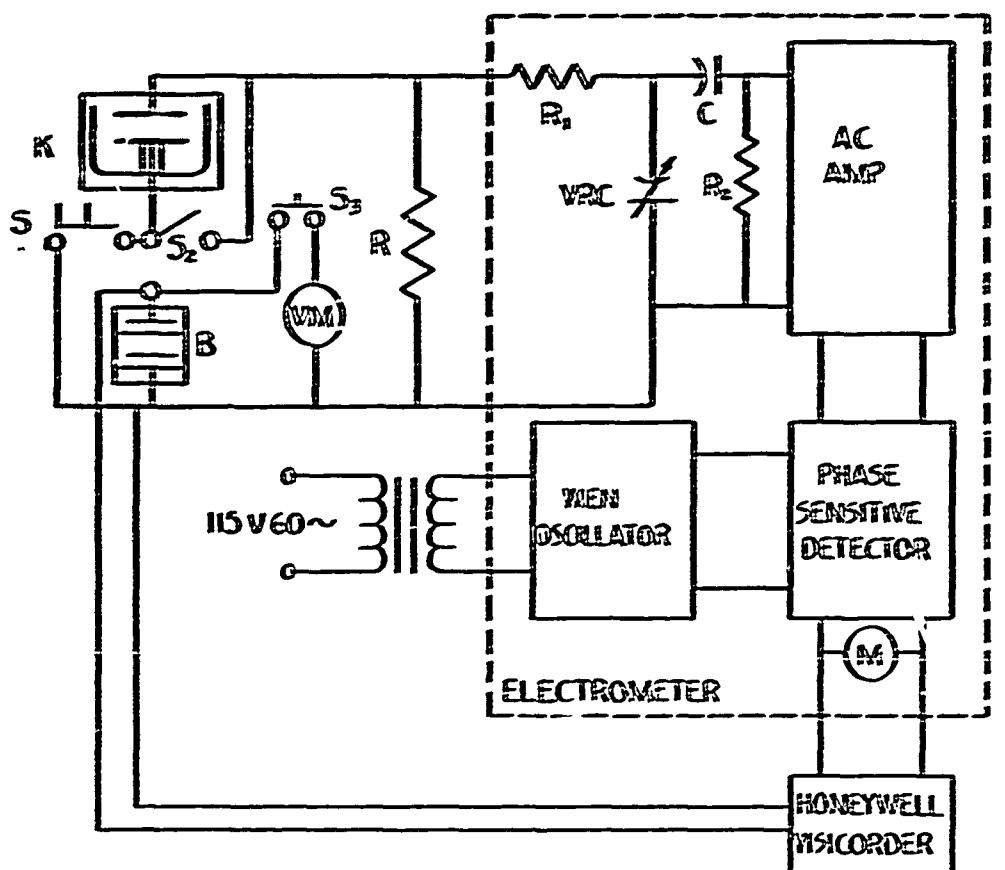
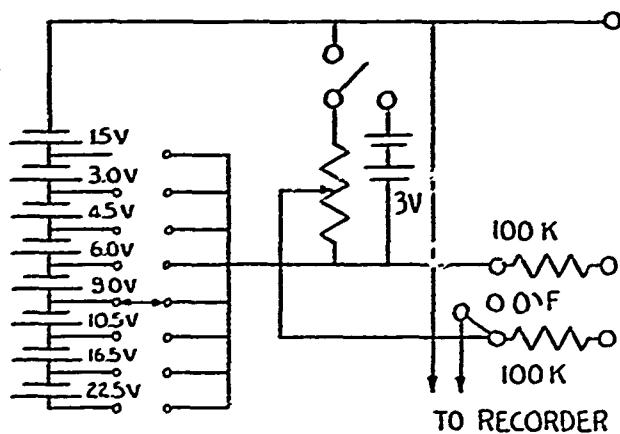


Fig. 1. Sectional View Conductivity Cell.



CONSTANT VOLTAGE POWER SUPPLY



B CONSTANT VOLTAGE
 SUPPLY
C COUPLING CAPACITOR
K CONDUCTIVITY CELL
VRC VIBRATING REED
 CAPACITOR
R₁, R₂ RESISTORS
R EXTERNAL RESISTOR
S, S₂, S₃, SWITCHES
T ISOLATION TRANSFORMER
 %VOLTAGE REGULATION
M MILLIVOLT METER

Fig. 2. Electrical Schematic Conductivity Cell.

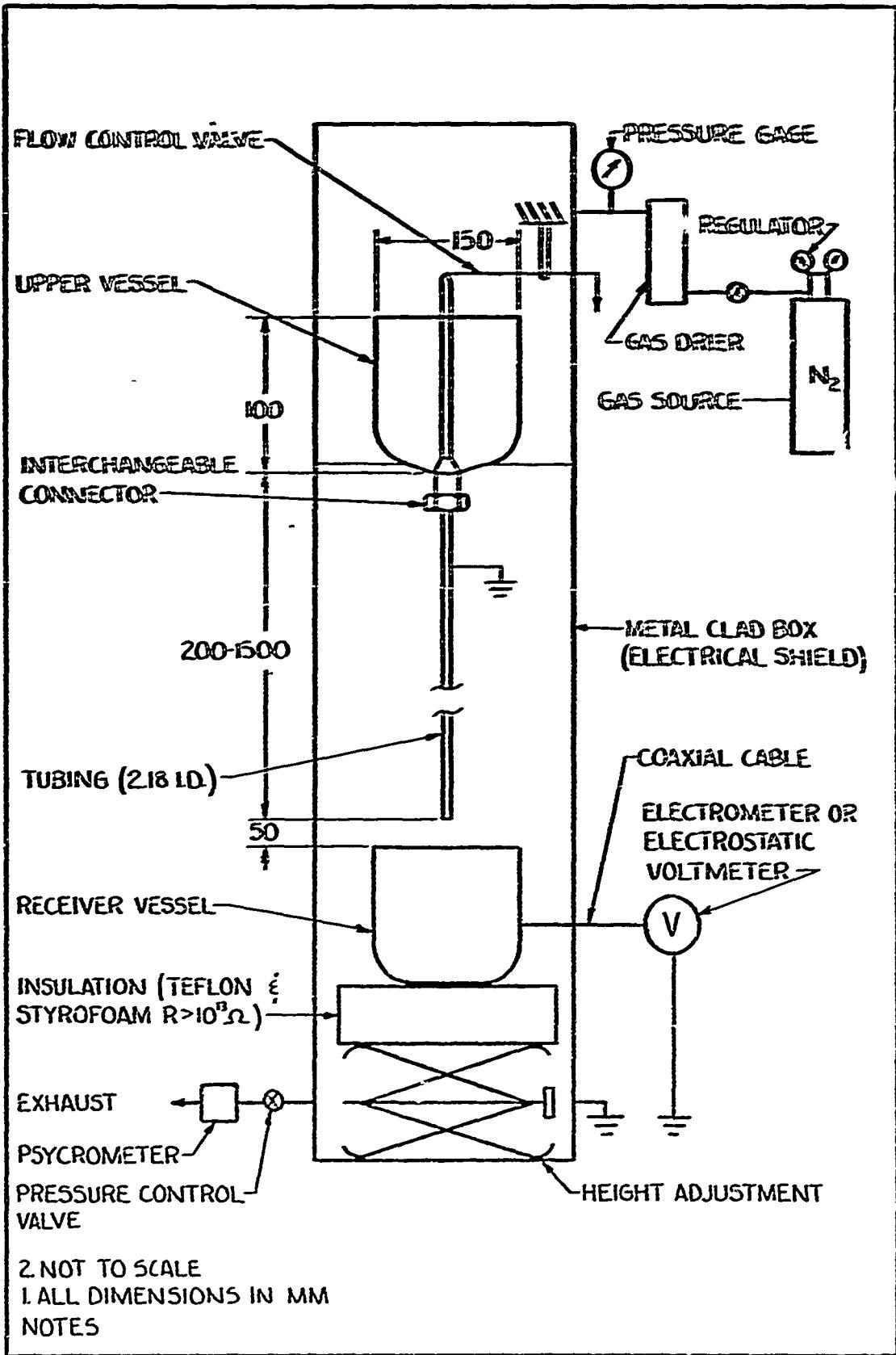


Fig. 3. Gravity Flow Charging Tendency Apparatus.

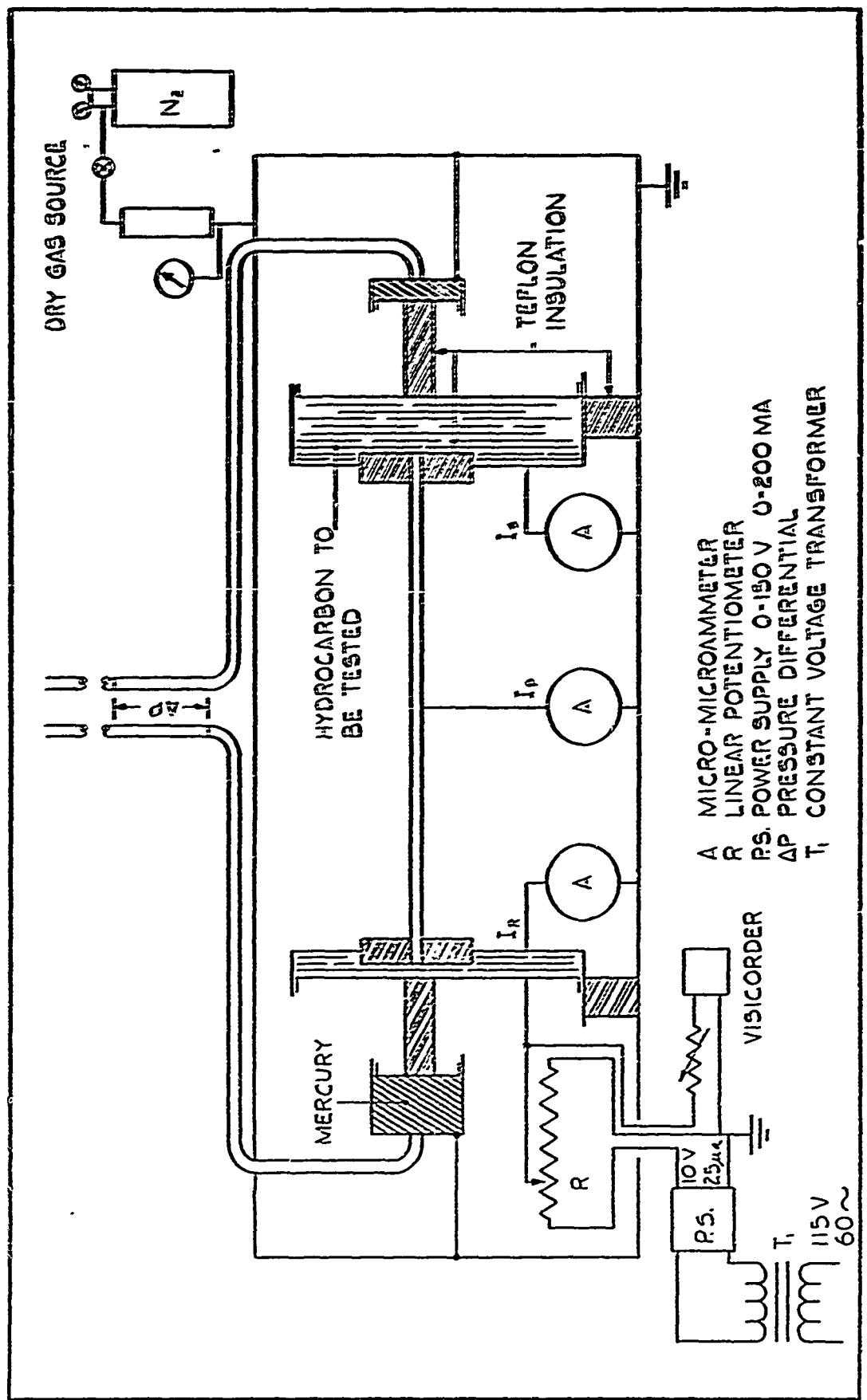


Fig. 4. Apparatus for Determining Static Charging in Full Pipelines.

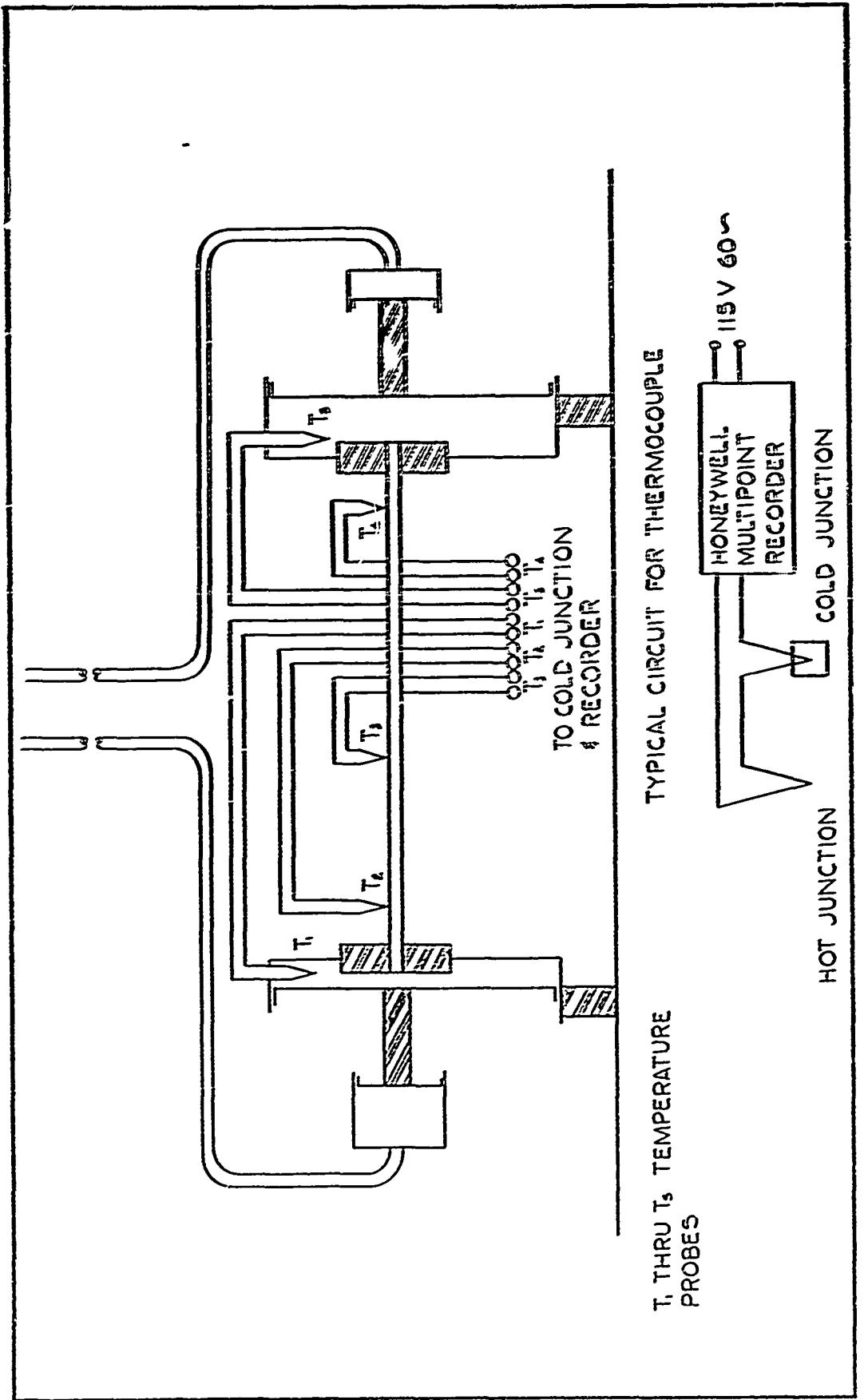
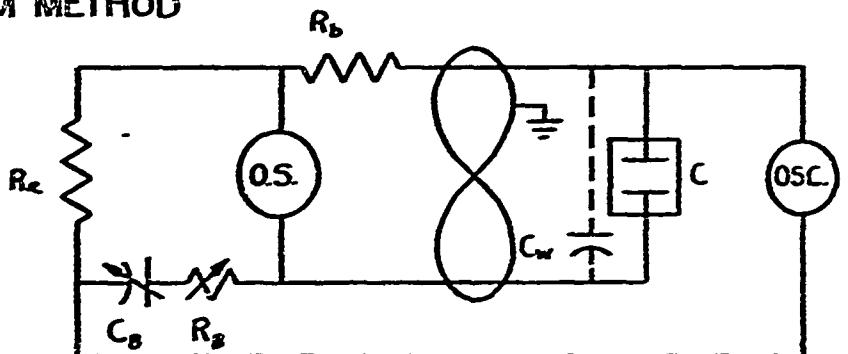


Fig. 5. Apparatus for Temperature Rise Determination.

ASTM METHOD



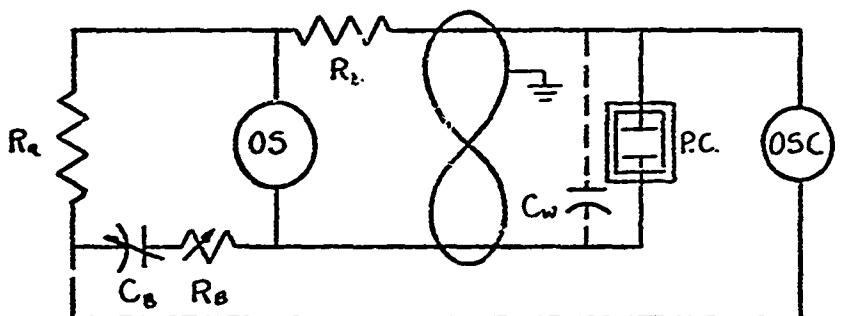
OSC 1000 HERTZ OSCILLATOR

OS. OSCILLOSCOPE

C CONDUCTIVITY CELL CAPACITANCE

C_b BRIDGE CAPACITANCE ADJUSTABLER_b, R_a, R_c BRIDGE RESISTORS ADJUSTABLEC_w CAPACITANCE OF CONNECTING WIRING

CAPACITANCE MEASUREMENT BY AC BRIDGE



OSC 1000 HERTZ OSCILLATOR

OS. OSCILLOSCOPE

P.C. PRECISION CAPACITOR OR SAMPLE CAPACITOR

R_b, R_a, R_c BRIDGE RESISTORSC_w CAPACITANCE OR CONNECTIVE WIRINGC_b BRIDGE CAPACITOR ADJUSTABLEFig. 6. Conductivity Cell Calibration by A.S.T.M.
AC Bridge Method.

Appendix B

Graphical Display of Preliminary Data

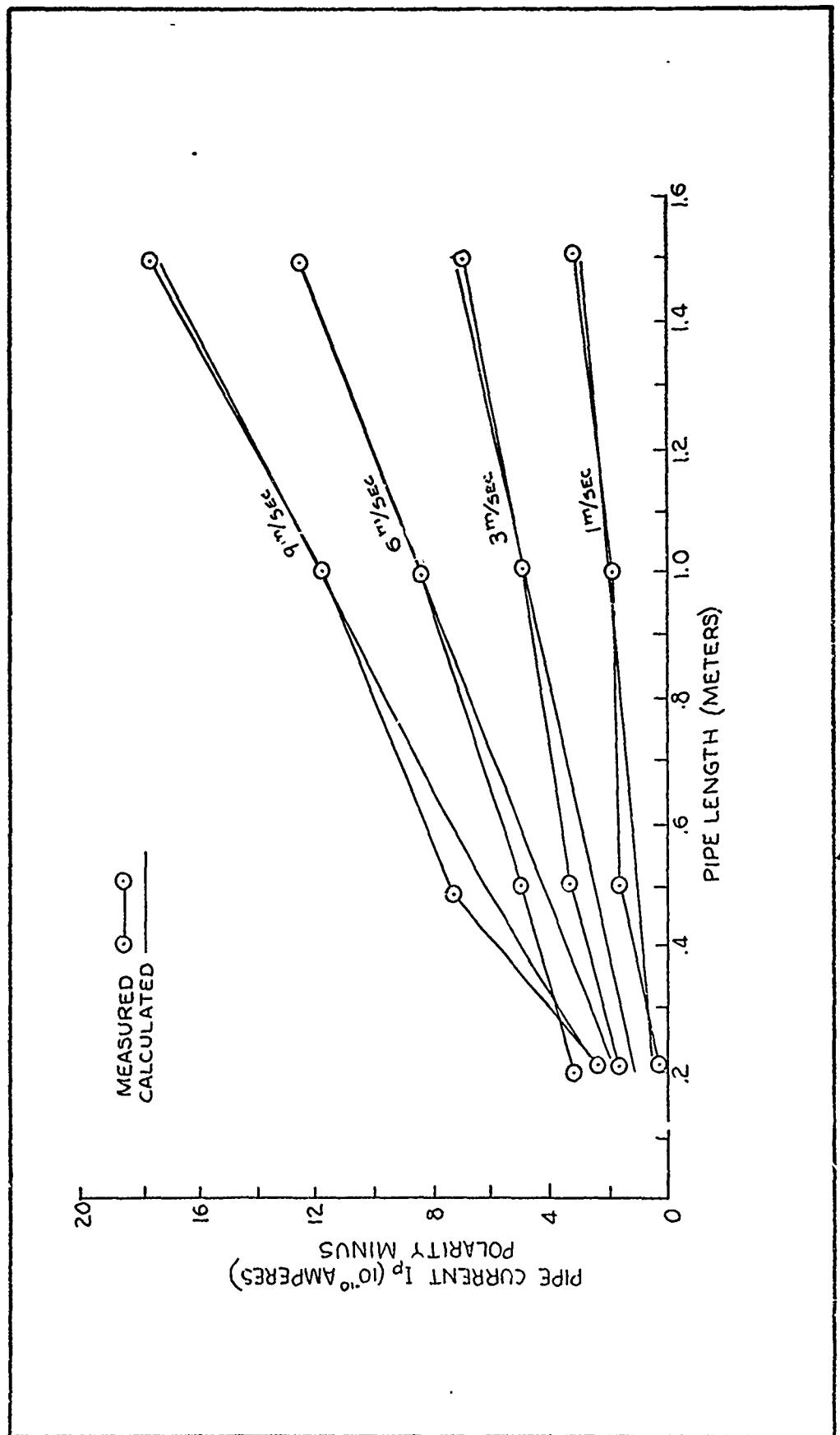


Fig. 7. The Effect of Pipe Length on Electrostatic Charging.

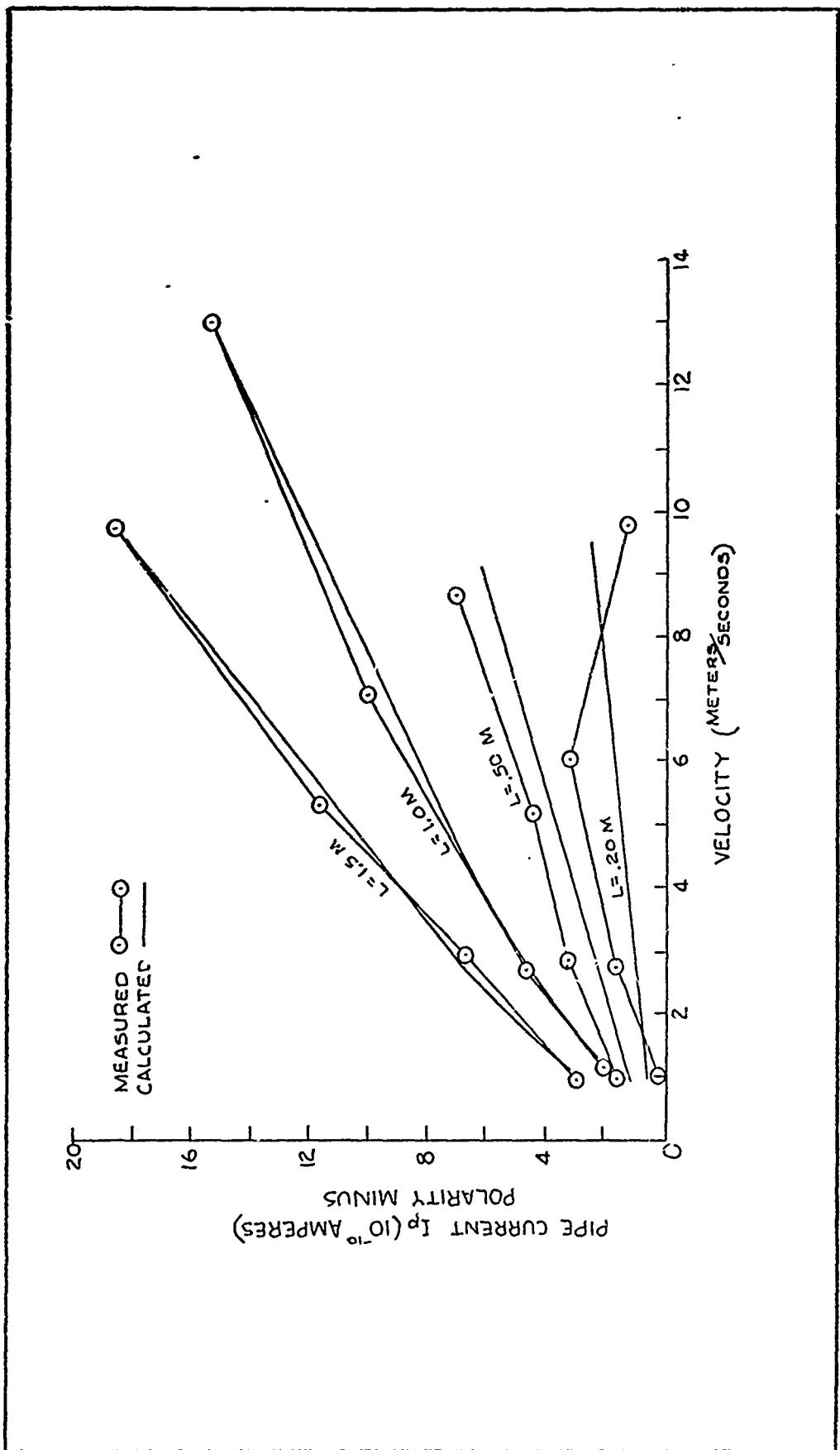


Fig. 8. The Effect of Velocity on Electrostatic Charging.

Appendix C

Operating Procedure and Equipment CalibrationConductivity Cell

For the determination of the conductivity, the value of capacitance of the empty vessel together with wiring and meters is required. This capacitance was determined using two methods, one similar to that described by Klenkenberger (Ref 3) and the other a proposed ASTM method outlined in a preliminary working document of ASTM Committee D-2 (Ref 7). The latter method was considered the best and most accurate and, therefore, adopted for use in this investigation. Figures 6 and 9 provide the circuit schematic diagrams.

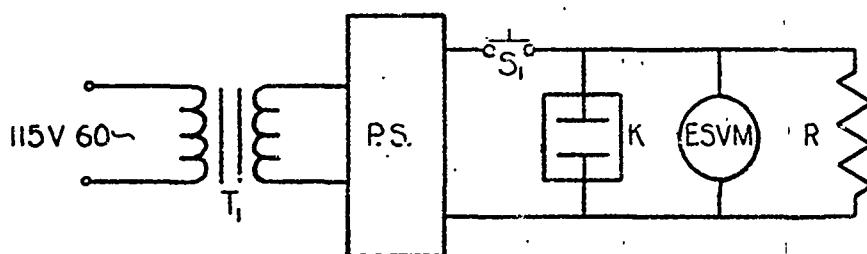
This procedure is considered the direct method as it uses a precision alternating current bridge to measure the cell's capacitance under various operating conditions. First, the cell is configured exactly as it will be used and the capacitance is measured with the sample chamber empty.

Figure 6 provides wiring diagram. Next the cell capacitance is measured in the exact same configuration as the first test but the sample container is filled to the proper depth with a hydrocarbon with a known dielectric constant. Cyclohexane was used for the standard hydrocarbon.

If we use C_e for capacitance of the empty cell and C_f the capacitance of the cell with hydrocarbon dielectric, then the active C' is given by

KLINKENBERG METHOD

STEP 1



T_1 , CONSTANT VOLTAGE TRANSFORMER

P.S. POWER SUPPLY 0-150V DC 200 MA

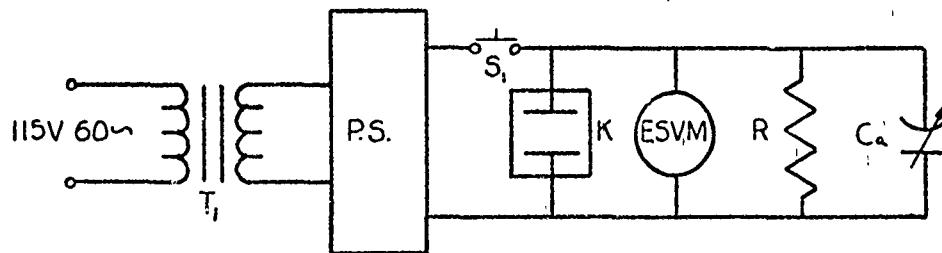
K CONDUCTIVITY CELL

S_1 , SWITCH "MOMENTARY ON"

ESVM ELECTROSTATIC VOLTMETER 0-150 VOLTS

R H-I MEG RESISTOR $10^6 \Omega$

STEP 2



T_1 , CONSTANT VOLTAGE TRANSFORMER

P.S. POWER SUPPLY 0-150 V DC 200 MA

K CONDUCTIVITY CELL

S_1 , SWITCH "MOMENTARY ON"

ESVM ELECTROSTATIC VOLTMETER 0-150 VOLTS

R HI-MEG RESISTOR $10^6 \Omega$

C_a 80 PF CAPACITOR

Fig. 9. Klenkenberg Method Conductivity Cell
Calibration.

$$C' = \frac{C_f - C_e}{\epsilon_H - 1} \quad (33)$$

where ϵ_H is the relative dielectric constant (2.013) of Cyclohexane standard. The cell constant, which is nothing more than the ratio of the distance between electrodes to the effective area for a parallel plate capacitor, is given by

$$K_c = \frac{\epsilon_0}{C'} \quad (34)$$

or

$$K_c = \frac{1}{11.26C'} \quad (35)$$

Calibration of Thermocouples and Multipoint Recorder

The calibration procedure used for this equipment was the standard method described by Coxon (Ref 8). The multipoint recorder which utilizes a nulled bridge circuit was modified for use with thermocouples prior to its application to this project.

Calibration of the Gravity Flow Charging Tendency Apparatus

The capacitance of the insulated receiving vessel including the wiring and voltmeter must be determined since the charge tendency is equal to the product of the capacitance and the potential of the receiver. The system used to make the determination is based on a measurement of the rate of decay of the potential across the capacitor. See Fig. 10 for details of equipment layout.

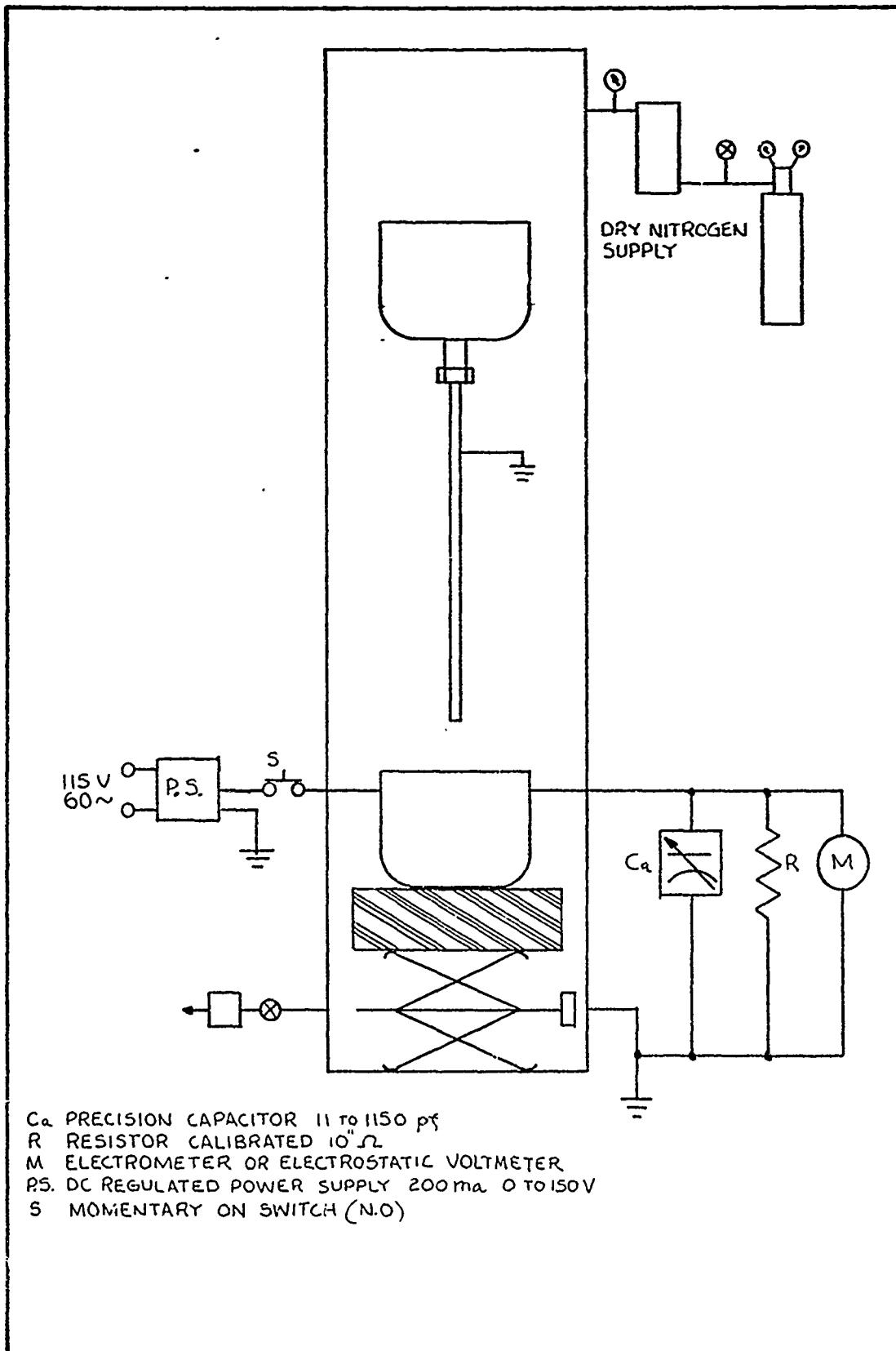


Fig. 10. Calibration Setup Charging Tendency Apparatus.

The insulated receiving vessel with all the wiring and meters attached is charged to about 150 volts using a direct current power supply. The apparatus is then allowed to discharge through a high resistance (10^{11} ohms) while the time, t_1 , required to reach one half the original potential is recorded. This same process is repeated, only this time the voltmeter is shunted with a capacitor of known value C_a and low leakage. The size of this capacitor is determined by the discharge time which can be accurately measured. The increment of time t_2 which is the time required for the potential to reach one half at original value is measured.

To calculate the capacitance C_R of the receiving vessel

$$C_R = \frac{t_1}{t_2 - t_1} C_a \quad (36)$$

The fluid velocity was determined from the inside diameter of the tube and the time required for a measured quantity of fuel to flow from the upper vessel to the receiver. This velocity was determined only for comparison purposes.

Calibration of Current Measuring Equipment

To measure currents whose magnitude is less than 10^{-12} amps requires special equipment and careful calibration with the particular external circuitry to be used. There is no set procedure to accomplish this. The manufacturer of the particular equipment used normally provides detailed instructions on matching impedance, measuring contact resistance,

and proper guard circuits. Many operating manuals place these instructions in an area called equipment performance specifications.

All electrometers used in this investigation were carefully evaluated in accordance with manufacturers instructions to insure their performance was within published specifications when used in a particular circuit.

Calibration of the Piston Travel Timer

In order to determine the current carried by a fluid flowing through a pipe the fluid velocity must be accurately known. This required the calibration of the linear potentiometer circuit used to determine the time of travel of the piston.

The piston travel distance was accurately defined by a measured distance between two stops. Then, a voltage applied to the potentiometer circuit will provide a zero slope line on the recorder corresponding to that voltage associated with the position of the stop. Only source voltage variations will appear in the slope of the line (scaled by the percentage of the potentiometer in the circuit) as long as the piston remains against the stop. Motion of the piston away from the stop will cause an abrupt change in the slope which will indicate start of time. Likewise at the end of travel the slope of the trace will again return to zero rather abruptly.

The selection of a record speed to accomplish this is governed by the piston velocity and the desired accuracy.

As the speed of the piston increases the travel time decreases so an increase in record speed improves both readability and accuracy. Considering the entire range of piston velocities and the record speeds normally available on most instruments, a record speed ten times faster than the piston speed appeared to be most workable.

Operating Procedure for Gravity Flow Charging Tendency

Apparatus

The apparatus is cleaned in accordance with the procedure outlined in Appendix D. To determine cleanliness highly purified xylene is run through the apparatus. System is considered clean when the charge generated by this pure hydrocarbon is less than 1 micro coulomb per cubic meter.

The actual development and procedure for the use of the apparatus is attributed to the Roy Dutch Petroleum Company Research Laboratories (Ref 3). A condensed description of their procedure is provided here.

The upper container is filled with one liter of liquid under investigation. If the conductivity of this liquid is less than 0.1 picomho/meter the liquid is allowed to relax at least ten minutes. The valve is opened and the liquid is allowed to flow under only the forces of gravity from the upper container into the receiving vessel. The voltage of the receiving container is determined using an electrostatic voltmeter of high time constant. A large potential difference is not desired between the receiver and the tube, therefore, the meter is shunted with a calibrated variable capacitor.

This will minimize leakage current through the free jet.

The procedure just described is repeated at least three times and the mean value of the voltage calculated. The mean value of the voltage multiplied by the total capacitance of the receiver (measured capacitance plus any shunt capacitance included) provides the charging tendency, S. In symbols

$$S = KVC \quad (37)$$

where K is a proportionality constant to compensate for units.

Appendix D

Preparation and Cleaning of Apparatus

The preparation and cleaning procedure established in this section was used on all three pieces of apparatus after each had undergone an initial cleaning process. The size of the part, the type of material and the condition when received governed the initial cleaning method.

Initial Cleaning Methods

The following procedures were used to clean parts either during manufacture or immediately after receipt:

- a. All teflon and polyethylene parts were kept as clean as possible during machining. Tools used were all washed in dry acetone as were the parts themselves.
- b. All metal parts were processed through a hot vapor degreaser and then washed in dry acetone.
- c. The silver plated electrodes were cleaned in a warm mixture of equal parts of nitric and hydrochloric acids.

Final Cleaning Process

The final cleaning process is used prior to all tests, however, some of the following procedures may be omitted or reduced in the number of times repeated depending on the experience of the operator and order in which samples are to be tested.

- a. The smaller parts with irregular surfaces were cleaned in an ultrasonic bath of dry acetone.

b. The parts were then flushed at least five times with a 2:1 ratio, mixture of alcohol and benzene, followed by a single flush with reagent grade acetone.

c. Between each flushing, the parts are dried with clean dry nitrogen.

d. Immediately before use, all parts which contact the sample are flushed with xylene a minimum of three times. Again, any residue is evaporated from the surface using clean dry nitrogen.

e. The liquid to be examined is used as the final rinse. The procedure is to allow the liquid to flow over all surfaces, which will be submerged during the test, at least three times. Nitrogen drying is not required but instead parts are allowed to thoroughly drain before a new quantity of the test liquid is introduced.

f. The procedures described in b and d may be replaced by a chloroform rinse repeated a minimum of five times.

Test for Cleanliness

All three pieces of apparatus must be checked for cleanliness by running an actual test. In the case of the conductivity cell, a run is made with a purified liquid of known conductivity which is lower than the range of the liquid being investigated. Cleaning is continued until the known value is reached within acceptable experimental error.

Alternate Special Methods

The literature indicates that the following special methods of cleaning were used on certain occasions:

a. The silver electrodes may be initially cleaned by using the reverse of the plating process. In this method the electrodes are placed in an electrolyte solution and a very thin layer of the surface removed by electrochemical action. Triplely distilled water is used to rinse any residue off the electrodes.

b. A method referenced in the literature but only used when measuring very low conductivities is that of surface outgassing and electrical cleaning. It applies only to the conductivity cell and is accomplished by placing a potential of several hundred volts between the electrodes (actual magnitude determined by electrode separation) and maintaining it for several hours. The electrolyte used is the liquid to be investigated. This process is followed by at least three rinses with the test liquid.

Vita

Valentine L. Denninger was born 4 September 1933 in Belrose, New York, the son of Valentine L. and Helen B. Denninger. He was graduated from high school in 1951, and entered Stevens Institute of Technology. In 1955 he was graduated from Stevens with a degree in Bachelor of Science in Mechanical Engineering and was commissioned in the Air Force as a result of the ROTC Program. After entering active duty and completing navigator training he was assigned to Military Air Transport Service for seven years as a transport navigator. In 1962 he was transferred into the Civil Engineering career field with his first assignment as Chief of Engineering and Design, Dover Air Force Base. After an assignment to SEA, he was made Director of Engineering and Construction for the Military Airlift Command at Scott Air Force Base. After four years in this capacity he was assigned to the Air Force Institute of Technology in the Graduate Astronautical Engineering program.

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This thesis was typed by Jane Manemann.